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Specification and Drawings, as originally filed, with Application for Patent Serial No:
2,435,779, on July 22, 2003, by **INSTITUT NATIONAL DE LA RECHERCHE
SCIENTIFIQUE**, assignee of Mario Bergeron and Marc Richer-Lafèche, for "A Process for
Recovering Platinum Group Metals from Ores and Concentrates".

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ABSTRACT OF THE DISCLOSURE

[0099] Disclosed is a process for recovering substantially all platinum group metals using a dry carbochlorination process. The feed material is amended with NaCl and subjected to the action of chlorine and carbon monoxide gases in an open furnace at temperature varying from about 250 °C to about 720 °C. The platinum, palladium, rhodium, ruthenium and iridium values remain in the solid material while the osmium values are carried in the gas phase exiting the reactor. Osmium is recovered from the gas phase, containing also FeCl₃, by the separate condensation of FeCl₃ in a condenser and the percolation of the exhaust condenser gas in water or HCl solutions. The platinum, palladium, rhodium, ruthenium and iridium are recovered from the solid material after the carbochlorination step by digestion in water or in diluted HCl solutions. The dissolved platinum group metals are extracted from the leached solutions by cementation or ions exchange resins. The process can be run simultaneously with the removal of iron from the feed as gaseous FeCl₃. Advantageously, where the feed is chromite rich, the recovery of the platinum group metals by the present process also conducts to an increase in the chromium to iron ratio of the feed, this ratio being directly related to the commercial value of chromites.

TITLE OF THE INVENTION

A PROCESS FOR RECOVERING PLATINUM GROUP METALS FROM ORES AND CONCENTRATES

FIELD OF THE INVENTION

[0001] The present invention relates to a process for recovering platinum group metals from ores and concentrates. More particularly, the present invention relates to the conversion of platinum group metals in highly soluble chloride complexes that can be recovered from solutions.

BACKGROUND OF THE INVENTION

[0002] Chromites and platinum group metals occur in potential association in specific geological environments such as stratified and layered mafic to ultramafic magmatic complexes that have intruded continental rocks. The term "platinum group metals", usually referring to the metals platinum, palladium, iridium, ruthenium, rhodium, osmium, are collectively designated hereinafter as "PGM". PGM rich chromitites are an extremely interesting ore because of their double economic values as: 1) a source of chrome for ferrochromium production, a master ferro-alloy for the stainless steel industry and 2) a source of metals for the PGM industry.

[0003] Presently, there are only a few large mining producers that operate metallurgical facilities capable of extracting PGM from chromitites, and these producers are all based in the Republic of South Africa (RSA). The PGM extraction process of RSA, Vermaak 1995, is based on: 1) the production of flotation concentrates which are then submitted to 2) smelting, 3) converting, 4) base metal extraction and 5) PGM purification. This PGM extraction process requires the production of a flotation concentrate and the development of a large metallurgical infrastructure. When considering the large variety of mineralogical composition of the phases carrying the PGM in chromites deposits, their grain-sizes distribution and the PGM concentration, the prospect of efficiently producing a flotation concentrate from chromite ores is often very limited. In addition, building a metallurgical infrastructure based

on smelter and on associated technologies is costly and not economically adapted to the extraction of PGM from small and medium scales deposits.

[0004] Bergeron, Lafèche, 2003a, United States copending patent application filed on February 7, 2003 discloses a method for carbochlorinating chromites. In that process, a chromite ore or a chromite concentrate mixed with NaCl is contacted with chlorine and carbon monoxide in a reactor maintained at temperatures of 250 °C to 720 °C to convert the iron oxide in the ore to gaseous iron chloride which is removed and condensed. The chemical reaction at the heart of the process is: $\text{FeO} \cdot \text{Cr}_2\text{O}_3 + 1.5\text{Cl}_2(\text{g}) + \text{CO}(\text{g}) \Rightarrow \text{Cr}_2\text{O}_3 + \text{FeCl}_3(\text{g}) + \text{CO}_2(\text{g})$. The solid material resulting from the process shows: 1) a large increase in its chromium to iron ratio; and 2) a residual enrichment in bulk Cr_2O_3 content. Both effects boost it's the ore's trading value.

[0005] The chromite ore used in the disclosed carbochlorination examples of Bergeron and Lafèche 2003a also possessed PGM values. This is not surprising as chromitites are often reported to be associated with or to contain PGM values.

[0006] Carbochlorination is a known process. The carbochlorination of chromites lead to the formation of gaseous FeCl_3 (ex. Bergeron and Lafèche, 2003a). A bibliographic study realized by Kanari, Ph. D. thesis Polytechnic Institut of Lorraine, 1995, on the formation of gaseous chlorides demonstrated that some chloride compounds are transported at temperatures where their partial vapor pressure is near zero. These materials contained Al and Fe compounds. It is well known that a transport involving gaseous iron chlorides or aluminum chlorides was at the origin of this phenomenon. Iron chlorides and aluminum chlorides can formed, with chlorides of other metals, compounds of the type $\text{M}_x\text{N}_y\text{Cl}_z$ (M= rare earths, precious metals, base metals, etc. N= Fe, Al, Ga and In). Kanari 1995, reported a complete list of references involving the formation of $\text{M}_x\text{N}_y\text{Cl}_z$ compounds. It is clear that chloride compounds can be volatilized at low

temperature in the presence of FeCl_3 or AlCl_3 . The present invention teaches the effect of formation of FeCl_3 on the vapor transportation of PGM and teaches a new process for the recovery of PGM from chromite ores. Prior to the present invention, those effects were not known.

[0007] When referring to gaseous chlorine metallurgy, three broad fields can be considered. The carbochlorination field that includes experiments, processes conducted with gaseous chlorine in the presence of a reductant such as carbon monoxide, usually chooses for process development, or coke. The chlorination field implies the use of chlorine in experiments or processes without adding a reductant material or gases. The field, chlorination in the presence of a salt melt, implies the formation of a molten bath of salt, by addition of a large quantity of salt, with or without the evolution of gaseous chlorine. The carbochlorination, the chlorination and chlorination in the presence of a salt melt are chemical processes involving different chemical reactions.

[0008] The literature on PGM recovery by gaseous chlorination from chromite ores is reviewed in accordance with the definition of these three fields. The effect of carbochlorination on PGM values contained in chromites was never disclosed. Certain effects of carbochlorination on PGM for other types of ores, concentrates, metallurgical products and materials were known:

Carbochlorination

[0009] The result of carbochlorination on PGM values contained in spent automotive catalyst are described in the prior art. Rivarola et al., 1981, Lat. Am. J. Chem. Eng. Appl. Chem., 11, 47-52, describe the volatilization of platinum from Al_2O_3 spent catalyst by a chlorine-carbon monoxide mixture. The recovery of platinum, as a volatilized phase, yielded extraction closed to 100 %. The influence of temperature, time, and gas flow rates were investigated.

[0010] United States Patent 5,102,632 Allen et al., 1992, relates to a method of recovering platinum, palladium and rhodium dispersed on ceramic support structures. The process involves two steps. In a first step a reducing chlorination is carried out during which the palladium and platinum are volatilized as chlorides. In a second step only chlorine is used to volatilize rhodium trichloride.

[0011] Kim et al., 2000, Ind. Eng. Chem. Res., 39, 1185-1192, report on the carbochlorination of spend automotive catalyst to extract the platinum and rhodium values. After optimization of time, temperature, gas flow rates, partial pressures of chlorine and carbon monoxide, recovery of 95 % of platinum and 92 % of rhodium were obtained.

Chlorination.

[0012] Extraction of PGM by chlorination from sulphides flotation concentrates was investigated by Cooper and Watson, as early as 1929, J. Chem. Metal. Min. Soc. S. A., 220-230. According to their procedure, a sulphides flotation concentrate is roasted, mixed with 15-20 % of NaCl and chlorinated at 550 °C for six hours. After the chlorination step, the solid is leached with concentrated HCl, PGM are cemented with zinc dust and the solution is filtered to isolate a PGM concentrate.

[0013] South African Patent 96-2382, Lalancette and Bergeron, 1996, describes the chlorination of chromites ore for the extraction of PGM. The statements of the invention implies mixing the ore with NaCl wt10%, dry chlorination of the mixture between 350 °C to 800°C with gaseous chlorine, dissolution of PGM in concentrated hydrochloric acid solution, filtering and recovering the PGM from the solution. PGM recoveries are reported to be in the order of 95 to 100 %.

[0014] Canadian Patent 2,303,046 Prior, 1999, teaches on the extraction of PGM from a material resulting from the smelting of sulphides

concentrates rich in base metals. The material is subjected to three gaseous treatments, an oxidizing treatment, a reducing treatment and a chlorination treatment at elevated temperature. After the gaseous treatments, the material is leached with HCl or aqua regia and the precious metals recovered by a chromatographic procedure.

[0015] Canadian Patent 2,314,581 Craig and Grant, 2000, describes a procedure for the removal of base metals especially the amphoteric elements present in metallurgical concentrates containing 60 wt % and more of precious metals. The presence of the base metals in the precious metals concentrates being considered as detrimental to the down stream refining steps. The procedure refers in order to the steps of: a) a high temperature treatment of the concentrate with gaseous HCl b) a treatment of the residue, if desirable, with chlorine gas, c) a high temperature treatment of the residue with oxygen, d) a high temperature treatment of the residue with hydrogen. This procedure minimizes losses of precious metals during the removal of the amphoteric elements.

Salt melt chlorination.

[0016] United States Patent No. 5,074,910 Dubrovsky, 1990, teaches the recovery of precious metals from base metals sulphide ores by chlorination in a molten salt bath in the presence of chlorine gas. The charge is pressed into pellets with addition 50 % of weight as salt, feeded to a reactor and contacted with chlorine gas at temperature producing a molten salt bath. After the complete conversion of the precious metals to chlorides, the precious metals are then recovered from the melt by a suitable means.

[0017] United States Patent No. 5,238,662 Dubrovsky, 1993 describes the recovery of precious metals contained in a matte obtained from the smelting of sulphide concentrates rich in base metals. The matte is contacted with gaseous chlorine in a molten salt bath to effectively convert the PGM to their chlorides forms. A novel selective dissolution technique for PGM involving multiple dissolution stages is also presented.

[0018] It is therefore known that

- A. PGM values are often associated with or contained in chromites;
- B. The carbochlorination of chromites result in the formation of FeCl_3 , this gaseous compound being able to form complexes with numerous metallic chlorides;
- C. Volatilization of PGM metals present in chromites can be affected by the presence of FeCl_3 thus resulting in their distribution in different process streams;

Prior to the present invention however, no data existed on the behaviour of platinum group metals during the carbochlorination of PGM rich chromites;

Existing data on PGM carbochlorination for other materials are limited to spend catalyst; and

Processes based on chlorination and salt melt chlorination for PGM recovery from ore, minerals and metallurgical concentrates involve different chemical reactions than carbochlorination, thus PGM recoveries are based on distinct methods.

[0019] Hence, there is a need to develop a process that can extract PGM from ores and concentrates including chromites. This process should be adaptable to a situation where a chromite is subjected to an enrichment process as described by Bergeron and Lafleche, 2003a by which the iron is extracted as gaseous FeCl_3 . This treatment could desirably be designed in such way that it could be run simultaneously with the enrichment of chromites as described by Bergeron and Lafleche 2003a.

SUMMARY OF THE INVENTION

[0020] It was surprisingly discovered that the action of chlorine and carbon monoxide resulted in the dissolution of PGM in slightly acidic solution. The effect of carbochlorination on the potential recovery of PGM in chromites is of great economic interest. According to specific embodiments of the present invention therefore, there is provided a process able to recover PGM

from chromite ores, and simultaneously remove of iron, using a similar approach. Hence, a process for the extraction of PGM linked to an increase in the chromium to iron ratio of chromites will raise the value of the starting chromite ore by combining, to the chromium resources, the PGM income. Also, in the process of the present invention, the production of a flotation concentrate is not required, thus ores otherwise identified as not presenting economical value can be brought into production. In such a process, the PGM are considered as a by-product, a consequence of the iron removal from chromites by carbochlorination.

[0021] According to specific embodiments of the method of the present invention, the reagents therefore provided a process to extract PGM metals from chromites avoiding the multiple steps of flotation, smelting, converting and autoclave leaches currently used by the PGM industries.

[0022] According to specific embodiments of the method of the present invention, the enrichment of chromites and the PGM extraction may be linked, therefore increasing the total value of the ore.

[0023] According to specific embodiments of the method of the present invention by which the mineralogical phases carrying the PGM may be converted to chloride complexes highly soluble in a slightly acidic solution.

[0024] According to specific embodiments of the method of the present invention the PGM may be extracted from the chromites with assistance of a catalyst system, which increase the kinetic of the reaction and the solubility of the PGM chemical species obtained by the process.

[0025] According to specific embodiments of the method of the present invention, the process including steps to insure the secure disposal of the residue.

[0026] According to specific embodiments of the method of the

present invention, the process includes steps by which the majority of the employed reagents may be recycled.

[0027] Other objects and further scope of applicability of the present invention will become apparent from the detailed description given hereinafter. It should be understood, however, that this detailed description, while indicating preferred embodiments of the invention, is given by way of illustration only, since various changes and modifications within the scope of the invention will become apparent to those skilled in the art.

[0028] This process is based, in parts, on the procedure by Bergeron and Lafleche 2003a on the removal of iron from chromites by carbochlorination in order to increase the chromium to iron ratio of chromites. PGM extraction chromites is performed with additional steps.

[0029] The present invention is advantageously applicable to chromite ores and different types of concentrates including alluvial chromites and PGM concentrates. If concentrates are used as feed to the invention, the concentrates can be obtained, after grinding of the ore, by the use of standard mineral processing technologies such as jigs, spirals, flotation units and multi-gravity separator.

[0030] According to a specific embodiment, there is provided a method for recovering platinum group metals (PGM) from a feed material selected from the group consisting of chromite ore, chromite ore concentrate and PGM concentrate comprising a) dry chlorinating the material, having a homogenous grain-size, in a reactor maintained at a temperature of between about 250°C and about 750°C in the presence of a NaCl-FeCl₃ system acting as a catalyst so as to produce a solid material, a gaseous phase containing FeCl₃, and PGM chlorine salts that are soluble in water and HCl, whereby a portion of the PGM chlorine salts are contained in said solid material, and another portion of the PGM chlorine salts are contained in said gaseous phase; and b) recovering PGMs from the PGM-chlorine-salts-containing solid material.

[0031] In a more specific embodiment, there the method further comprising the step of recovering PGMs from the PGM-chlorine-salts-and- FeCl_3 -containing gaseous phase. The steps of recovering PGMs from the PGM-chlorine-salts-containing solid material and of PGMs from the PGM-chlorine-salts-and- FeCl_3 -containing gaseous phase can be performed sequentially or simultaneously.

[0032] According to an other specific embodiment, the method of the present invention comprise steps similar those contained in the procedure on the carbochlorination of chromites by Bergeron and Laflèche 2003a in addition to steps directed to the PGM recovery. Those additional steps are identified as such below.

[0033] The method of the present invention comprises the steps of:

- a) grinding a material selected from the group consisting of chromite ore, chromite ore concentrate and PGM concentrate, to an average grain size of about 125 μm to yield a homogeneous grain-size feed;
- b) contacting the feed with a mixture of salt of different compositions in a concentration of about 5 % (w/w) to about 15% (w/w) to yield a treated feed, this mixture acting as a catalyst for the chlorination reactions. In specific embodiments the mixture of salts comprises NaCl in a concentration of about 5 % (w/w) to about 15% (w/w) ;
- c) drying and/or pre-heating the treated feed at about 180° C to yield a dried feed. In specific embodiments, this step is conducted for about 30 minutes to about 2 hours;
- d) reacting the dried feed from c) with chlorine (Cl_2) and carbon monoxide (CO) at temperatures varying from about 250° to about 720° C in chlorination reactor. In specific embodiments, the chlorination reactor is a furnace built with material resistant to chlorine for a period of time

varying from about 30 minutes to about two hours, to yield a gaseous FeCl_3 stream and a solid material from which the iron has been extracted, and to convert PGM into PGM chlorides complexes salts;

- e) condensing the FeCl_3 gaseous stream obtained from d) in a suitable condenser to yield a FeCl_3 concentrate and a gas phase , where FeCl_3 can be recovered from the FeCl_3 by washing with water and yield aqueous FeCl_3 -- FeCl_3 being highly soluble in water-;

Additional step f)

- f) contacting the gas phase with water or a solution of hydrochloric acid to yield a leached solution and residual chlorine gas. In specific embodiments, the HCl has a molarity varying between about 0.1 and about 3 M HCl . ; when HCl solutions are employed, only a small quantity of HCl is consumed, the HCl solutions can therefore be recycled if desirable;
- g) reacting residual chlorine gas with metallic iron scrap and washing water in order to obtain aqueous FeCl_3 ;
- h) combining streams of aqueous FeCl_3 of e) and g) in an agitated reservoir;
- i) neutralizing, from the combined streams of aqueous FeCl_3 of h) by adding NaOH in order to obtain aqueous NaCl and an iron oxide precipitate;
- j) separating the NaCl and the iron oxide precipitate to obtain an iron oxide cake and a clear NaCl solution, the iron oxide cake being disposable in a regulated tailing pound;
- k) electrolyzing the NaCl solution of j) to regenerate Cl_2 and NaOH. The chlor-alkali membrane cell process but other suitable methods may be used, the reaction products being : Cl_2 , NaOH and H_2 .

- l) advantageously, the Cl_2 and NaOH generated in steps d) and l), respectively may be recycled as reactants for the chlorination and neutralization reactions and H_2 generated in step k) may be recycled as additional combustible for the chlorination reactor;

Additional steps m) to p)

- m) contacting the solid material of step d) with water or a solution of hydrochloric acid of various molarities in an agitated reservoir to yield a leached solution. In more specific embodiments, HCl may vary between about 0.1 to about 3 M HCl . This contact may be performed for about 10 to about 20 minutes; the agitation step may include heating or boiling the mixture; typically the ratios (w/w) of water/enriched solid material or HCl /enriched solid material vary between about 2.5 to about 50; when HCl solutions are employed, only a small quantity of HCl is consumed, the HCl solutions can be therefore recycled if desirable; alternatively the solid material obtained from step d) is contacted, in a similar manner, directly with the leached solution of step f);
- n) separating the solid material from the leached solution of step m) containing dissolved PGM chemical species to yield a solid residue and a solid impoverished leached solution;
- o) recovering the PGM values from the leached solutions isolated in steps f) and n) by zinc cementation or by the utilization of appropriate ion exchange resins;
- p) advantageously, the HCl solution may be recycled or a HCl 6 M solution regenerated by distillation, this latter solution being used to prepare the HCl solution having a molarity of about 0.1 to about 3 M.

[0034] According to an other specific embodiment, there is provided a method for the extraction of PGM from a starting feed selected from the group consisting of chromite ore, chromite ore concentrate and PGM concentrate comprising the steps of:

- a) grinding the starting feed to an average grain size of about 125 μm to yield a homogeneous grain-size feed;
- b) adding to the homogenous feed NaCl in a concentration of between about 5 % to about 15% (w/w);
- c) drying the feed resulting of step b) to a temperature of about 180 °C for about 30 minutes to yield a dry feed process free of water and containing NaCl (w/w);
- d) reacting the dried feed process with a gaseous mixture of Cl_2 and CO at a temperature range varying between about 250° and about 750° C in a suitable chlorination reactor to yield a solid residue and a gaseous phase, and wherein:
 - i) PGM phases present in the chromites react with Cl_2 , CO and NaCl to produce PGM chlorides salts that are soluble in water and HCl solutions; and
 - ii) FeCl_3 is produced by the reaction $\text{FeO} \cdot \text{Cr}_2\text{O}_3 + 1.5\text{Cl}_2(\text{g}) + \text{CO}(\text{g}) \Rightarrow \text{Cr}_2\text{O}_3 + \text{FeCl}_3(\text{g}) + \text{CO}_2(\text{g})$ and carried outside the reactor by the flow thru of the gaseous phaseand wherein a portion of the PGM chlorine salts are contained in said solid residue, and another portion of the PGM chlorine salts are contained in the gaseous phase;
- e) condensing the FeCl_3 in a condenser to yield a FeCl_3 condensate and a gaseous phase;
- f) washing the FeCl_3 condensate with water to yield an aqueous solution rich in FeCl_3 ;
- g) quenching the gaseous phase in an agitated reservoir containing water or a HCl solution of varying molarities to yield a leached

solution containing PGMs, Cl_2 and CO ;

- h) recovering the PGM of step g) by an appropriate method such as zinc cementation or ions exchange resins;
- i) digesting the solid residue in water or in a HCl solution of varying molarities in an agitated reservoir maintained at a temperature of about 70°C to yield a digested mixture;
- j) separating the mixture of step i) to obtain:
 - i) a solid residue showing an increase in its chromium to iron ratio as compared to that of the starting feed and;
 - ii) a leached solution containing dissolved PGM species;
- k) drying the solid residue of step j);
- l) recovering the PGM from the leached solution of step J) by an appropriate method such as zinc cementation or ions exchange resins;
- m) reacting Cl_2 of step g) with scrap of metallic iron to yield an aqueous solution rich in FeCl_3 , CO being burned with air to yield gaseous CO_2 ;
- n) neutralizing the aqueous solutions rich in FeCl_3 of steps f) and g) with NaOH by the reaction $\text{FeCl}_3(\text{aq}) + 3\text{NaOH}(\text{aq}) \Rightarrow \text{Fe}(\text{OH})_3(\text{s}) + 3\text{NaCl}(\text{aq})$ to yield a solution containing NaCl and an iron hydroxides precipitate;
- o) separating the aqueous NaCl solution from the iron hydroxides precipitate by a suitable solid-liquid separation method to yield a clear aqueous NaCl solution and a iron hydroxides cake filter, this latter product being disposable in a tailing pound; and
- p) electrolyzing the NaCl solution to regenerate Cl_2 and NaOH .

[0035]

According to a further specific embodiment, there is

provided a method for the extraction of PGM from a starting feed selected from the group consisting of chromite ore, chromite ore concentrate and PGM concentrate wherein the extraction of FeCl_3 is minimised or is not occurring. It includes the steps of:

- a) grinding the starting feed to an average grain size of about $125\ \mu\text{m}$ to yield a homogeneous grain-size feed;
- b) adding to the homogenous feed NaCl in a concentration of between about 5 % to about 15% (w/w);
- c) drying the feed resulting of step b) to a temperature of about $180\ ^\circ\text{C}$ for about 30 minutes to yield a dry feed process free of water and containing NaCl (w/w);
- d) reacting the dried feed process with a gaseous mixture of Cl_2 and CO at a temperature range varying between about 250° and about 750°C in a suitable chlorination reactor to yield a solid residue and a gaseous phase, and wherein:
 - i) PGM phases present in the chromites react with Cl_2 , CO and NaCl to produce PGM chlorides salts that are soluble in water and HCl solutions; and
 - ii) the reaction $\text{FeO} \cdot \text{Cr}_2\text{O}_3 + 1.5\text{Cl}_2(\text{g}) + \text{CO}(\text{g}) \Rightarrow \text{Cr}_2\text{O}_3 + \text{FeCl}_3(\text{g}) + \text{CO}_2(\text{g})$ is minimised or not occurring so that no FeCl_3 is carried outside the reactor by the flow thru of gases;and wherein a portion of the PGM chlorine salts are contained in said solid residue, and another portion of the PGM chlorine salts are contained in the gaseous phase;
- e) quenching the gaseous phase of step d) in an agitated reservoir containing water or HCl solutions of varying molarities to yield a leached solution containing PGMs, Cl_2 and CO;
- f) recovering PGMs from the leached solution of step e) by an appropriate method such as zinc cementation or ions exchange

resins;

- g) digesting the solid residue of step d) in water or in a HCl solution of varying molarities in an agitated reservoir maintained at a temperature of about 70°C to yield a digested mixture;
- h) separating the mixture of step i) to obtain:
 - i) a solid residue; and
 - ii) a leached solution containing dissolved PGM species;
- i) drying the solid residue of step h);
- j) recovering PGM species from the leached solution of step h) by an appropriate method such as zinc cementation or ions exchange resins;
- k) reacting Cl_2 of step e) with scrap of metallic iron to yield an aqueous solution rich in FeCl_3 , CO being burned with air to yield gaseous CO_2 ;
- l) neutralizing the aqueous solutions rich in FeCl_3 of step k) with NaOH by the reaction $\text{FeCl}_3(\text{aq}) + 3\text{NaOH}(\text{aq}) \Rightarrow \text{Fe}(\text{OH})_3(\text{s}) + 3\text{NaCl}(\text{aq})$ to yield a solution containing NaCl and an iron hydroxides precipitate;
- m) separating the aqueous NaCl solution from the iron hydroxides precipitate by a suitable solid-liquid separation method to yield a clear aqueous NaCl solution and a iron hydroxides cake filter, this latter product being disposable in a tailing pound; and
- n) electrolyzing the NaCl solution to regenerate Cl_2 and NaOH.

[0036] According to another specific embodiment, there is provided a method for the extraction of PGM from a starting feed selected from the group consisting of chromite ore, chromite ore concentrate and PGM concentrate including the steps of:

- a) grinding the starting feed to an average grain size of about 125 μm to yield a homogeneous grain-size feed;
- b) adding to the homogenous feed NaCl in a concentration of between about 5 % to about 15% (w/w);
- c) drying the feed resulting of step b) to a temperature of about 180 $^{\circ}\text{C}$ for about 30 minutes to yield a dry feed process free of water and containing NaCl (w/w);
- d) reacting the dried feed process with a gaseous mixture of Cl_2 and CO at a temperature range varying between about 250 $^{\circ}$ and about 750 $^{\circ}$ C in a suitable chlorination reactor to yield a solid residue and a gaseous phase, and wherein:
 - i) PGM phases present in the chromites react with Cl_2 , CO and NaCl to produce PGM chlorides salts that are soluble in water and HCl solutions; and
 - ii) FeCl_3 is produced by the reaction $\text{FeO} \cdot \text{Cr}_2\text{O}_3 + 1.5\text{Cl}_2(\text{g}) + \text{CO}(\text{g}) \Rightarrow \text{Cr}_2\text{O}_3 + \text{FeCl}_3(\text{g}) + \text{CO}_2(\text{g})$ and carried outside the reactor by the flow thru of the gaseous phase
and wherein a portion of the PGM chlorine salts are contained in said solid residue, and another portion of the PGM chlorine salts are contained in the gaseous phase;
- e) condensing the FeCl_3 in a condenser to yield a FeCl_3 condensate and a gaseous phase;
- f) washing the FeCl_3 condensate with water to yield an aqueous solution rich in FeCl_3 ;
- g) quenching the gaseous phase in an agitated reservoir containing water or a HCl solution of varying molarities to yield a leached solution containing PGMs, Cl_2 and CO;
- h) digesting the solid residue in the quenching solution of step g) in an agitated reservoir maintained at a temperature of about 70 $^{\circ}\text{C}$ to yield a digested mixture;
- i) separating the mixture of step i) to obtain:
 - i) a solid residue showing an increase in its chromium to iron ratio

as compared to that of the starting feed and;

ii) a leached solution containing dissolved PGM species;

- j) drying the solid residue of step j);
- k) recovering PGM species from the leached solution of step i) by an appropriate method such as zinc cementation or ions exchange resins;
- l) reacting Cl_2 of step g) with scrap of metallic iron to yield an aqueous solution rich in FeCl_3 , CO being burned with air to yield gaseous CO_2 ;
- m) neutralizing the aqueous solutions rich in FeCl_3 of step l) with NaOH by the reaction $\text{FeCl}_3(\text{aq}) + 3\text{NaOH}(\text{aq}) \Rightarrow \text{Fe}(\text{OH})_3(\text{s}) + 3\text{NaCl}(\text{aq})$ to yield a solution containing NaCl and an iron hydroxides precipitate;
- n) separating the aqueous NaCl solution from the iron hydroxides precipitate by a suitable solid-liquid separation method to yield a clear aqueous NaCl solution and a iron hydroxides cake filter, this latter product being disposable in a tailing pound; and
- o) electrolyzing the NaCl solution to regenerate Cl_2 and NaOH.

[0037] According to another specific embodiment, there is provided a method for the extraction of PGM from a starting feed selected from the group consisting of chromite ore, chromite ore concentrate and PGM concentrate including the steps of:

- a) grinding the starting feed to an average grain size of about 125 μm to yield a homogeneous grain-size feed;
- b) adding to the homogenous feed NaCl in a concentration of between about 5 % to about 15% (w/w);
- c) drying the feed resulting of step b) to a temperature of about 180 °C for about 30 minutes to yield a dry feed process free of water and containing NaCl (w/w);
- d) reacting the dried feed process with a gaseous mixture of Cl_2 and CO

at a temperature range varying between about 250° and about 750° C in a suitable chlorination reactor to yield a solid residue and a gaseous phase, and wherein:

i) PGM phases present in the chromites react with Cl_2 , CO and NaCl to produce PGM chlorides salts that are soluble in water and HCl solutions; and

ii) the reaction $\text{FeO} \cdot \text{Cr}_2\text{O}_3 + 1.5\text{Cl}_2(\text{g}) + \text{CO}(\text{g}) \Rightarrow \text{Cr}_2\text{O}_3 + \text{FeCl}_3(\text{g}) + \text{CO}_2(\text{g})$ is minimised or not occurring so that no FeCl_3 is carried outside the reactor by the flow thru of gases;

wherein a portion of the PGM chlorine salts are contained in said solid residue, and another portion of the PGM chlorine salts are contained in the gaseous phase;

- e) quenching the gaseous phase of step d) in an agitated reservoir containing water or HCl solutions of varying molarities to yield a leached solution containing PGMs, Cl_2 and CO;
- f) digesting the solid residue in the quenching solution of step e) in an agitated reservoir maintained at a temperature of about 100°C to yield a digested mixture;
- g) separating the mixture of step f) to obtain:
 - i) a solid residue; and
 - ii) a leached solution containing dissolved PGM species;
- h) drying the solid residue of step g);
- i) recovering PGM species from the leached solution of step g) by an appropriate method such as zinc cementation or ions exchange resins;
- j) reacting Cl_2 of step e) with scrap of metallic iron to yield an aqueous solution rich in FeCl_3 , CO being burned with air to yield gaseous CO_2 ;
- k) neutralizing the aqueous solutions rich in FeCl_3 of step j) with NaOH

by the reaction $\text{FeCl}_3(\text{aq}) + 3\text{NaOH}(\text{aq}) \Rightarrow \text{Fe}(\text{OH})_3(\text{s}) + 3\text{NaCl}(\text{aq})$ to yield a solution containing NaCl and an iron hydroxides precipitate;

l) separating the aqueous NaCl solution from the iron hydroxides precipitate by a suitable solid-liquid separation method to yield a clear aqueous NaCl solution and a iron hydroxides cake filter, this latter product being disposable in a tailing pound; and

m) electrolyzing the NaCl solution to regenerate Cl_2 and NaOH.

[0038] According to a more specific embodiment, the starting feed is a chromite ore.

[0039] According to an alternative more specific embodiment, the starting feed is a chromite concentrate obtained by a suitable mineral processing technology.

[0040] According to an alternative more specific embodiment, the starting feed is a PGM concentrate obtained by a suitable mineral or metallurgical processing technology such as a flotation concentrates and metallurgical mattes.

[0041] According to another more specific embodiment, about 5% (w/w) of NaCl is added in step b).

BRIEF DESCRIPTION OF THE DRAWINGS

[0042] Figure 1 illustrates a flow diagram of a specific embodiment of the present invention in which the PGM are collected in two separate leaching solutions.

[0043] Figure 2 illustrates a flow diagram of a specific embodiment of the present invention in which the PGM are collected in one leaching solution.

DESCRIPTION OF SPECIFIC EMBODIMENTS

[0044] Referring to figures 1 and 2, the feed to the process can be the direct ore or an ore concentrate obtained from an appropriate mineral processing technology.

MIXING.

[0045] The ore or concentrate is mixed with a solution of NaCl to obtain, after drying, a feed containing 5 % NaCl by weight. The combined action of NaCl and FeCl₃, created during the carbochlorination step, causes the formation of a eutectic point in the system NaCl-FeCl₃. This mixture acts as a catalyst for the chlorination reactions. More details on this system and pertinent references are reported in Bergeron and Lafleche, 2003a. In general, the salt addition produces a thin liquid film around each grain. This liquid film contains a strong chlorination agent such as: 1) NaFeCl₄ resulting from the reaction of FeCl₃ with NaCl or 2) dissolved iron species acting as chlorine supplier to the chlorination sites. Hence, Zao, Tian and Duan (1990, Metallurgical Transactions B, 21B, pp. 321-330) have reported from experiments in molten salt bath that the chlorine transport to the reaction sites proceeded via the reaction: $\text{FeCl}_{2(\text{melt})} + 0.5\text{Cl}_{2(\text{gas})} = \text{FeCl}_{3(\text{melt})}$; the chlorine pressure decreasing rapidly at the reaction site, causing the decomposition of FeCl₃ and formation of FeCl₂ which, by reaction with external chlorine, turns again to FeCl₃. In practice, the carbochlorination reactions occur in a micro molten salt bath.

[0046] In the specific case of PGM, the addition of NaCl will also produce PGM chloride salts of the type Na₂PtCl₆, Na₂PdCl₄, Na₃RhCl₆, Na₂IrCl₆, etc., which are highly soluble in water or in diluted hydrochloric acid (Pascal, 1958, Nouveau traité de chimie minérale, Masson et Cie, Tome 19, pp. 949).

DRYING AND PRE-HEATING.

[0047] The drying step will ensure a complete removal of water resulting from the salt addition and can be carried out at different temperatures and time periods. In a specific embodiment, the charge was dried at 180 °C for 30 minutes. After cooling, the charge was transferred in the chlorination reactor and pre-heated at the selected reaction temperature.

CARBOCHLORINATION.

[0048] The teachings of Pascal, 1958 show that all PGM react with gaseous chlorine to form chlorides compounds at temperature generally above 240 °C. Highly soluble metallic salts of PGM can then be derived from the chlorides compounds when these are contacted with NaCl. The pertinent information from Pascal 1958 on the formation of metallic salts of PGM is reported below for each of the metal composing the PGM. The formation of PGM chloride salts is thought to be desirable to avoid the formation of volatile chloride such as PtCl_2 and PdCl_2 and their escape in different process streams.

Platinum.

[0049] Pascal, 1958, p. 744 to 752, reports the formation of platinum complexes with chlorides for the valence 1, 2, 3, and 4. Heating platinum sponge in a chlorine atmosphere or contacting the metal with hot chlorine p. 744 and 745 forms the complexes PtCl_2 (240 °C), PtCl_3 (350 °C) and PtCl_4 (600 to 850 °C). PtCl_3 can also be obtained from PtCl_2 by heating in a chlorine atmosphere at 390-400 °C, p. 745. Metallic salts derive from the platinum chlorides complexes include Na_2PtCl_4 , Na_2PtCl_6 , the latter is formed by heating PtCl_4 with NaCl. According to Pascal, 1958, the complexes Na_2PtCl_4 , Na_2PtCl_6 are highly soluble in water, p. 782.

Palladium.

[0050] Pascal, 1958, p. 612 to 613 reports the formation of PdCl_2 when palladium sponge is contacted with chlorine gas at 300 °C, the complex

is sublimed on the cold parts of the reaction tube. The salt Na_2PdCl_4 , highly soluble in water, is obtained by the contact of PdCl_2 with a NaCl solution, p. 631.

Rhodium.

[0051] Pascal, 1958, p. 325 reports the formation of RhCl_3 when the finely devised metal is contacted with chlorine at 300°C . The reaction kinetic increases with temperature up to 950°C , point after which the complex is decomposed to RhCl_2 and RhCl , p. 324. The salt Na_2RhCl_6 is prepared by passing chlorine gas on a mixture of rhodium and NaCl, the obtained salt is highly soluble in water, p. 335.

Iridium.

[0052] Pascal, 1958, p. 495 reports on the formation of IrCl_3 by contacting the metal with chlorine at temperature ranging from 600 to 620°C . IrCl_3 is stable in a chlorine atmosphere at temperatures up to 760°C . From $763^\circ\text{C} < t < 773^\circ\text{C}$ IrCl_2 is obtained and from $773^\circ\text{C} < t < 798^\circ\text{C}$ IrCl is formed. The chlorination of iridium is greatly improved when carried out with the addition of CO to the gaseous chlorine. Na_2IrCl_6 is prepared by the action of hot chlorine (dark red) on iridium mixed with NaCl, p. 502. This iridium salt is very soluble in water.

Ruthenium.

[0053] Pascal, 1958, p. 112 mentions the formation of RuCl_3 when the metal is heated in a Cl_2/CO atmosphere at 350°C . The complexes RuCl_2 and RuCl are not formed by contact of the metal with hot chlorine, p. 143, p. 164 or by the decomposition of RuCl_3 . The chlorination of ruthenium in the presence of NaCl, at low temperature, gives Na_2RuCl_6 , a complex soluble in water p. 89.

Osmium.

[0054] Pascal indicates that OsCl_4 is the principal product of the action of chlorine on the metal at 650 °C, p. 246. Na_2OsCl_6 is prepared by contacting chlorine with a mixture of the finely divided metal and NaCl, p. 253. The salt Na_2OsCl_6 is soluble in water.

[0055] During the carbochlorination step, the feed is contacted with chlorine, CO and NaCl in such a way to favour the formation of the PGM metallic salts. The catalytic system previously described in the present work and by Bergeron and Laflèche 2003a involving a molten salt bath of NaCl/ FeCl_3 containing dissolved gaseous Cl_2 appears ideally suited to form metallic salts of PGM. The examples presented below indicate that, except for osmium, the metallic salts of PGM do not escape from the molten salt bath and therefore are not present in other process streams.

[0056] The carbochlorination step is conducted in a horizontal static furnace at temperature varying from 250 °C to 720 °C. The chlorination reactions regarding PGM recovery can be run in two modes.

[0057] In the first mode the PGM are converted to metallic salts with simultaneous extraction of gaseous FeCl_3 . In such a case, the carbochlorination conditions are set to optimize the rate of FeCl_3 removal. Usually these conditions involve temperature in the range of 670 °C, Cl_2/CO ratio of one and a relatively high flow rate of 220 ml/min for both Cl_2 and CO.

[0058] In the second mode, the carbochlorination conditions are optimized for the conversion of PGM to metallic salts. In this case, the expulsion of FeCl_3 outside the reactor is minimised by using a low flow rate of about 20 ml/min for both Cl_2 and CO. To ensure optimal conversion of the PGM, the feed is maintained in contact with Cl_2 and CO for about 2 hours. The carbochlorination temperature is varied from about 320 °C up to about 720 °C depending on the nature of the ores or concentrates.

[0059] As stated in Bergeron and Laflèche 2003a, usually, at

industrial scale, carbochlorination is realized in fluidized bed reactor constructed of acid resistant bricks enclosed in a metal shell. The salt addition results in the formation of a thin liquid film layer around the chromite grains, which increases their adherence properties. It is therefore desirable to avoid fluidized reactor and the problems associated with grains agglomeration and bed sedimentation. Alternatively, a vertical static reactor can be used or an horizontal rotating reactor. Other obvious arrangements include the addition of solid reducing agents like coal, coke in replacement of CO. Pelletizing-sintering procedures, similar to the ones employed in the ferrochromium industry, can be done before the chlorination step.

[0060] After the chlorination reaction, the solid minerals contained in the reactor are dumped. Depending on the duration of the reaction, the gas flow rate, the salt additives, the Cl_2/CO mixture, the chlorinated solid residue shows an increase in its chrome to iron ratios and its PGM values have been converted to metallic salts.

CONDENSER

[0061] As stated in Bergeron and Laflèche 2003a, gaseous FeCl_3 exit continuously the reactor during the carbochlorination reaction. Outside the reactor, the temperature drops abruptly causing fast condensation of this product in the top section of the condenser. The condenser is placed at an adequate distance from the furnace so to keep its temperature below 50°C . FeCl_3 is highly soluble in water. A small volume of water is added to the condenser apparatus to wash the solid FeCl_3 . The FeCl_3 rich aqueous solution accumulates at the base of the condenser and is directed into a reservoir for subsequent neutralization. The other gases leaving the reactor are mainly Cl_2 , CO , CO_2 and N_2 . These gases are not affected by the presence of the condenser and flow through it without experiencing any changes in their compositions or states and exit the condenser.

DIGESTING REACTOR

[0062] The chlorinated solid residue is then placed in contact with water or a HCl solution having a molarity of about 0.1 to about 3 M in a digester. The pulp is agitated for about 15 minutes. If desirable, the solution is heated or boiled during the agitation period and the digester can be equipped with a condensing system. The HCl solution can be replaced by water. During the carbochlorination step, the osmium value is transported in the vapor phase and is not affected by the condensation of FeCl_3 .

QUENCHING OF THE VAPOR PHASES

[0063] The Os value exit therefore the condenser and is recovered by quenching the vapor phases, mainly composed of Cl_2 , CO, CO_2 and N_2 , with water or a HCl solution having a molarity of about 0.1 to about 3 M.

FILTRATION AND PGM RECOVERY

[0064] After the digestion procedure, the digester pulp is filtered. The solution containing the dissolved PGM salts is subjected to Zn cementation to recover a PGM concentrate. Alternatively, the PGM can be recovered by an ion exchange procedure. The solid phase isolated from the filtration process shows an increase in its chromium to iron ratio and can be commercialized, among other things, as a enriched chromite feed for a ferrochromium furnace.

[0065] The Os value contained in the quenching solution is recovered by Zn cementation. Similarly to the other PGM, the Os can be recovered by an ion exchange procedure.

[0066] In an alternate use of the process, the solution containing the quenched Os value is used to digest the solid residue obtained at the end of the carbochlorination step.

ACID REGENERATION

[0067] The process uses diluted HCl. Only a slight quantity of HCl

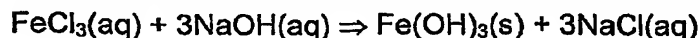
is consumed in the process. Hence, the HCl digesting solution can be recycled to the digester. The HCl solution can be re used until pH rises to a value diminishing the PGM solubility. A 6 M HCl solution can be regenerated by distillation. The pH of the digesting solution is adjustable to the required value by water dilution.

WASHING TOWER AND GAS TREATMENT

[0068] Cl_2 , CO, CO_2 and N_2 exiting the quenching solution, or the digesting reactor in the alternate version, are routed toward a washing tower. As stated in Bergeron and Laflèche 2003a; scraps of metallic iron in the millimeter range are placed in the tower and sprayed with a small quantity of water in order to keep wet the iron metallic surfaces. This arrangement favors the reaction $\text{Fe(s)} + 3/2\text{Cl}_2 \Rightarrow \text{FeCl}_3(\text{aq})$ which consume the unreacted Cl_2 . After the reaction, FeCl_3 is present as a solute in H_2O . CO and CO_2 percolate up and exit the washing tower near the top. CO is burned as CO_2 in an after burner unit. If required by environmental regulations, the scrubbing of CO_2 can be achieved by an existing complementary technology. The aqueous FeCl_3 solution flows out at the base of the washing tower to be routed toward the neutralization reservoir.

NEUTRALIZATION

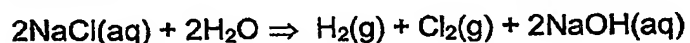
[0069] As stated in Bergeron and Laflèche 2003a, the aqueous FeCl_3 solutions coming from the condenser and the washing tower are pumped in a neutralization reservoir. A solution of NaOH is added to the tank. The ferric chloride reacts with NaOH according to the reaction:



[0070] After completion of the reaction, the solid amorphous iron oxides are isolated from the liquid phase by an appropriate solid-liquid separation such as centrifugation or press filtration. The filtration cake is discharged to the tailings. The aqueous NaCl solution is directed to an electrolysis cell.

ELECTROLYSIS

[0071] As described in copending US application by Bergeron and Laflèche 2003a, the NaCl solution, obtained from the neutralization section of the process, is electrolyzed by a chlor-alkali membrane cell process. The reaction involved is:



[0072] The gaseous Cl_2 and aqueous NaOH generated by the reaction are recycled in the process. The Cl_2 is returned to the carbochlorination reactor and the aqueous NaOH in the neutralization section. The $\text{H}_2(\text{g})$ produced by this reaction can be employed as the main energy source or an additional energy source for the carbochlorination furnace. If needed external supplies of NaCl can be used.

[0073] Any means for routing, transporting, and transferring solid, gas, liquid and pulp are within the scope of these inventions. The following inventions are commented in further details by the following non-limiting examples.

EXAMPLES

[0074] The following detailed examples are presented as specific illustrations of the presently claimed invention. It should be understood, however, that the specific invention is not limited to the specific details set forth in the Examples.

[0075] In the present case, the experiments were performed on a massive chromitite layer obtained from the Menarik deposit (James Bay, Quebec). The average mineralogy of 29 massive chromite layers of the Menarik Complex is: chromite 45 %, chlorite 32 %, serpentine 13 %, magnetite 3 %, talc 1 %, hornblende 4 % and traces of sulfides. The sample was hand-picked from the chromite mineralized zone Cr-1 and subsequently grinded to about 125 µm and homogenized. The individual concentrations of Pd, Pt, Ir, Rh, Ru and Os contained in the samples were analyzed by a nickel sulfide fire-assay procedure adapted to chromite followed by a finish by inductively coupled plasma mass spectrometry, ICP-MS. These concentrations were used as a reference point for the calculation of the PGM recovery during the carbochlorination experiments.

[0076] The major and complementary trace elements were analyzed by inductively coupled plasma atomic emission spectroscopy, ICP-AES, after a fusion procedure specifically applicable to chromite ore.

[0077] The implementation and results of the examples provided herein are summarized in Table 1. The carbochlorination experiments were carried out in a 65 cm in length horizontal cylindrical furnace equipped with a type K pyrometer linked to a thermostat controller. Usually, a 10 grams sample was placed in a ceramic boat and inserted in a silica-fused tube. The beaker-tube assembly was then introduced in the furnace. A glass tube was fitted to the tube exiting the furnace using a Teflon joint to extend the tube 0.5 meter outside the furnace. The condensate (condensate) is present in this external section of the tube. The vapor phase (gas phase), still present in the

extended tube, at room temperature, were contacted, in a vessel, with either water or 0.1 M to 3 M HCl. After the carbochlorination step, the solid contained in furnace (the residue) and the condensate were digested in either water or 0.1 M to 3 M HCl solutions. The residue, representing the solid present in the furnace after the experiment, the condensate, representing the gas condensed on the side of the tube and the gas phase, representing the vapor reaching the quenching vessel were analyzed separately for the PGM, see table 1 and figures 1 and 2.

Table 1. Examples of the recovery of PGM from the carbochlorination experiments.

| Notation | Remarks | Cl ₂ ml/min | CO ml/min | Cl ₂ /CO | T °C | Time H | Pd ppb | Pt ppb | Ir ppb | Os ppb | Rh ppb | Ru ppb |
|-------------------|------------------------------|---------------------------|--------------|---------------------|---------|-----------|-----------|-----------|-----------|-----------|-----------|-----------|
| CR-1a, NiS | Nickel sulphide fire-assay | | | | | | 1019 | 274 | 17 | 15 | 79 | 55 |
| CR-1b, NiS | Nickel sulphide fire-assay | | | | | | 1208 | 317 | 20 | 18 | 87 | 61 |
| CR-1d, NiS | Nickel sulphide fire-assay | | | | | | 1281 | 314 | 22 | 20 | 96 | 68 |
| CR-1 average | Nickel sulphide fire-assay | | | | | | 1169 | 301.7 | 19 | 18 | 87 | 61 |
| PGM-1, residue | 5% NaCl, 3 M HCl | 220 | 220 | 1 | 720 | 2 | 1122 | 248 | 31 | 2.9 | 94 | 114 |
| PGM-1, condensate | 5% NaCl, 3 M HCl | 220 | 220 | 1 | 720 | 2 | ND | ND | ND | ND | ND | ND |
| PGM-1, gas | 5% NaCl, 3 M HCl | 220 | 220 | 1 | 720 | 2 | 47 | 17 | <1 | 69 | <1 | <0.6 |
| PGM-1, TOTAL | 5% NaCl, 3 M HCl | 220 | 220 | 1 | 720 | 2 | 1169 | 265 | 31 | 72 | 94 | 114 |
| PGM-2, residue | 5% NaCl, 3 M HCl | 20 | 20 | 1 | 660 | 2 | 1091 | 320 | 21 | 1.7 | 84 | 85 |
| PGM-2, condensate | 5% NaCl, 3 M HCl | 20 | 20 | 1 | 660 | 2 | ND | ND | ND | ND | ND | ND |
| PGM-2, gas | 5% NaCl, 3 M HCl | 20 | 20 | 1 | 660 | 2 | 11 | 8 | <1 | 45 | <1 | <0.6 |
| PGM-2, TOTAL | 5% NaCl, 3 M HCl | 20 | 20 | 1 | 660 | 2 | 1102 | 328 | 21 | 47 | 84 | 85 |
| PGM-3, residue | 5% NaCl, digestion hot water | 200 | 200 | 1 | 660 | 2 | 624 | 149 | 25 | 2.3 | 69 | 45 |
| PGM-3, condensate | 5% NaCl, digestion hot water | 200 | 200 | 1 | 660 | 2 | ND | ND | ND | ND | ND | ND |
| PGM-3, gas | 5% NaCl, digestion hot water | 200 | 200 | 1 | 660 | 2 | 28 | 4 | <0.8 | 5 | <0.5 | <0.7 |
| PGM-3, TOTAL | 5% NaCl, digestion hot water | 200 | 200 | 1 | 660 | 2 | 652 | 153 | 25 | 7.3 | 69 | 45 |

ND: Not detected

Cr-1a to Cr-1d are sub-samples of the same starting ore.

PGM-1 to PGM-3 are different carbochlorination experiments.

Table 2. PGM recovery, %.

| Notation | Remarks | Cl ₂ ml/min | CO ml/min | Cl ₂ /CO | T °C | Time H | Pd % | Pt % | Ir % | Os % | Rh % | Ru % |
|-------------------|------------------------------|---------------------------|--------------|---------------------|---------|-----------|---------|---------|---------|---------|---------|---------|
| PGM-1, residue | 5% NaCl, 3 M HCl | 220 | 220 | 1 | 720 | 2 | 96 | 82 | 160 | 16 | 108 | 186 |
| PGM-1, condensate | 5% NaCl, 3 M HCl | 220 | 220 | 1 | 720 | 2 | ND | ND | ND | ND | ND | ND |
| PGM-1, gas | 5% NaCl, 3 M HCl | 220 | 220 | 1 | 720 | 2 | 4 | 6 | 0 | 388 | 0 | 0 |
| PGM-1, TOTAL | 5% NaCl, 3 M HCl | 220 | 220 | 1 | 720 | 2 | 100 | 88 | 160 | 404 | 108 | 186 |
| PGM-2, residue | 5% NaCl, 3 M HCl | 20 | 20 | 1 | 660 | 2 | 93 | 106 | 108 | 10 | 96 | 139 |
| PGM-2, condensate | 5% NaCl, 3 M HCl | 20 | 20 | 1 | 660 | 2 | ND | ND | ND | ND | ND | ND |
| PGM-2, gas | 5% NaCl, 3 M HCl | 20 | 20 | 1 | 660 | 2 | 1 | 3 | 0 | 253 | 0 | 0 |
| PGM-2, TOTAL | 5% NaCl, 3 M HCl | 20 | 20 | 1 | 660 | 2 | 94 | 109 | 108 | 262 | 96 | 139 |
| PGM-3, residue | 5% NaCl, digestion hot water | 200 | 200 | 1 | 660 | 2 | 53 | 49 | 129 | 13 | 79 | 73 |
| PGM-3, condensate | 5% NaCl, digestion hot water | 200 | 200 | 1 | 660 | 2 | ND | ND | ND | ND | ND | ND |
| PGM-3, gas | 5% NaCl, digestion hot water | 200 | 200 | 1 | 660 | 2 | 2 | 1 | 0 | 28 | 0 | 0 |
| PGM-3, TOTAL | 5% NaCl, digestion hot water | 200 | 200 | 1 | 660 | 2 | 56 | 51 | 129 | 41 | 79 | 73 |

Table 3. Major elements, Residue PGM-1, starting chromite.

| Sample | Total % | Al ₂ O ₃ % | C=O % | Fe ₂ O ₃ T % | K ₂ O % | MgO % | Na ₂ O % | P ₂ O ₅ % | S % | SiO ₂ % | TiO ₂ % | CaO % |
|-------------------|------------|-------------------------------------|----------|---------------------------------------|-----------------------|----------|------------------------|------------------------------------|--------|-----------------------|-----------------------|----------|
| Residue PGM-1 | 100.0 | 19.0 | .288 | 3.23 | .0870 | 17.5 | .357 | <0.21 | .0750 | 3.21 | .319 | 54.6 |
| Starting chromite | 101.5 | 12.7 | .166 | 25.3 | .0450 | 11.2 | .218 | <0.17 | .264 | 1.87 | .352 | 48.2 |

EXAMPLE 1

[0078] This example demonstrates that by using carbochlorination, in conditions promoting the formation of a large quantity of FeCl_3 , substantially all PGM may be recovered from the residue, except Os, which may be recovered from the gas phase. According to a specific embodiment, the process of the present invention may recover the PGM contained in these two streams.

[0079] A ten-gram sample of the chromite CR-1 was mixed with a NaCl solution. After drying, the salt content of CR-1 was 5 % by weight. This material was loaded in the reactor and the temperature was raised to 720 °C in the presence of N_2 . Once the reaction temperature was reached, 200 ml/min of Cl_2 and 200 ml/min of CO were flow through the reactor. The mixture of gas was maintained in contact with the solid for 2 hours. Ten minutes after the introduction of the gas mixture, the evolution of FeCl_3 exiting the reactor and condensing outside the reactor in the condenser area was noted. The gas phase escaping the condenser area was quenched in a 3 M HCl solution. No precipitate was noted in the quench vessel, although a red-yellow coloration appeared in the HCl solution. This quench solution was used as a trap for the PGM transported in the gas phase. During the run, the FeCl_3 evolution continued and no reduction was observed in the rate of formation of FeCl_3 .

[0080] After the two hours run, the reactor was cooled down to room temperature. Nitrogen was flushed in to the reactor during the cooling period. The solid left in the reactor, the residue, was transferred in a glass beaker and on a hot plate. One hundred ml of a 3 M HCl solution was added to the residue. The mixture was agitated for 15 minutes at 70 °C. After the agitation period, the mixture was filtered and the resulting clear solution was analysed for PGM by ICP-MS. The solid condensate (mostly FeCl_3) was recovered from the condenser area by washing with 3 M HCl. The condensate was digested using exactly the same digesting procedure as the one used for the residue. The quenching 3 M HCl solution used as a trap for the PGM

contained in the gas phase was analysed directly for the PGM.

[0081] Analysis of the condensate fraction by ICP-MS for the PGM did not lead to consistent results, most of the concentrations of PGM being below or close to detection limits. The poor detection limits were related to a matrix effect created by the high concentration of FeCl_3 in the analysed solution. Therefore, the presence of PGM in this particular fraction was estimated from the mass balance of the total PGM content.

[0082] The distribution of the PGM in the residue and in the gas phase are presented at the table 1 for the sample noted PGM-1. As may be seen from table 1, the sums of the PGM for the residue and the gas phase give for: Pd 1169 ppb, Pt 265 ppb, Ir 31 ppb, Os 72 ppb, Rh 94 ppb and Ru 114 ppb. The PGM concentrations obtained from the nickel sulphide fire-assay, reported at the table 1, can be used as the 100 % recovery mark. Hence, the sums of PGM values in the residue and the gas phases were recalculated as per cent recovery at the Table 2. The experimental error, including sample homogeneity, is in the order of ± 15 %. For Pd, Pt and Rh the recoveries are within 100 ± 15 % limits and are considered here as complete. For Ir, Ru and Os the recoveries exceeded 100 ± 15 % limits. Os is considered as being loss as OsO_4 during the fusion stage in the NiS fire-assay method. Therefore, it is not surprising that the recovered value by carbochlorination exceeded by a factor 4 the expected value in the starting ore. For Ir and Ru, the carbochlorination process appears to be a superior approach to NiS fire-assay for achieving complete dissolution of these two specific PGM in chromites. Losses of Ru as RuO_4 are also reported during the fusion stage. Nickel sulphide fire-assay shows limits when applied to chromite and often the slag must be refused to achieve complete recovery of PGM.

[0083] As may be seen from Tables 1 and 2, the process, according to specific embodiments, is able to achieve complete extraction of substantially all PGM from the feed. PGM are leached from the residue and

gas phase streams, losses of PGM to the condensate stream appear to be negligible.

[0084] One application of the present invention is a situation in which a simultaneous extraction of PGM is sought out with an increase in the chromium to iron ratio of the reacted chromite. In such a situation the economic value of the PGM is combined to the value of a chromite showing a high chromium to iron ratio. The carbochlorination conditions used in this example produces a high increase in the chromium to iron ratio of the reacted chromite. Hence, before the carbochlorination the Cr to iron ratio of the chromite was determined at 1.9 after the carbochlorination step, the chromium to iron ratio reached 16.9, see table 3 for major elements analysis.

[0085] Therefore, Tables 1 to 3 demonstrate that the process, according to specific embodiments is able to recover substantially all the PGM from a chromite ore. The PGM are only present in the residue and the gas phase (Os only) streams. The process can be run concurrently with a large removal of FeCl_3 . The removal of FeCl_3 produces an increase in the chromium to iron ratio of the chromite used as a feed to the process.

EXAMPLE 2

[0086] This example demonstrates that the extraction of PGM may be substantially complete in conditions where the carbochlorination does not involve a large loss of FeCl_3 and therefore the chromium to iron ratio of the chromite feed is not substantially modified after the process. Such a situation occurs in the case where only the extraction of the PGM from the feed is required. Because the PGM are present in the sample in trace amount, the consumption of Cl_2 required for the conversion of PGM carrying phases to PGM chloride salts is minimal. The reduction in Cl_2 consumption has an important impact on the process commercial viability.

[0087] These conditions also shorten the subsequent metallurgical steps since the quantity of FeCl_3 formed is very small is condensation,

neutralisation and disposition as $\text{Fe}(\text{OH})_3$ is simplified.

[0088] A ten-gram sample of the chromite ore CR-1 was contacted with a solution of NaCl. After drying the salt content of CR-1 was 5 % by weight. This material was loaded in the reactor and the temperature was raised to 660 °C in the presence of N_2 . Once the reaction temperature was reached, 20 ml/min of Cl_2 , 20 ml/min of CO and 100 ml/min of N_2 were flown through the reactor. The mixture of gas was maintained in contact with the solid for 2 hours. Contrary to example 1, only the formation of a very small quantity of FeCl_3 was noted during the length of the experiment. The gas phase escaping the condenser area was quenched in a 3 M HCl solution. No precipitate was noted in the quenching vessel, although a red-yellow coloration appeared in the HCl solution. This quenching solution was used as a trap for the PGM transported in the gas phase.

[0089] After the two hours run, the reactor was cooled down to room temperature. Nitrogen was flushed in to the reactor during the cooling period. The solid left in the reactor, the residue, was transferred in a glass beaker placed on a hot plate. One hundred ml of a 3 M HCl solution was added to the residue. The mixture was agitated for 15 minutes at 70 °C. After the agitation period, the mixture was filtered and the resulting clear solution was analysed for PGM by ICP-MS. The solid condensate (mostly FeCl_3) was recovered from the condenser area by washing with 3 M HCl. The condensate was digested using exactly the same digesting procedure as the one used for the residue. The quenching 3 M HCl solution, used as a trap for the PGM contained in the gas phase, was analysed directly for the PGM.

[0090] Analysis of the condensate fraction by ICP-MS for the PGM did not lead to consistent results, most of the concentrations of PGM being below or close to detection limits. The poor detection limits were related to a matrix effect created by the high concentration of FeCl_3 in the analysed solution and to the small mass of FeCl_3 recovered from the condenser. Therefore, the presence of PGM in this particular fraction was estimated from

the mass balance of the total PGM.

[0091] The distribution of the PGM in the residue and the gas phase are presented in Table 1 for the sample noted PGM-2. As may be seen from Table 1 the sums of the PGM for the residue and the gas phases give for: Pd 1102 ppb, Pt 328 ppb, Ir 21 ppb, Os 47 ppb, Rh 84 ppb and Ru 85 ppb. The PGM concentrations obtained from the nickel sulphide fire-assay, reported in Table 1, can be used as the 100 % recovery mark. Hence, the sums of PGM values in the residue and the gas phases were recalculated as per cent recovery in Table 2. The experimental error is in the order of ± 15 %. For Pd, Pt, Ir and Rh the recoveries are within 100 ± 15 % limits and are considered here as complete. For Ir, Ru and Os recovery are higher than 100 %. Similarly as in example 1, recoveries higher than 100 ± 15 % are attributed to the superiority of the carbochlorination process to extract PGM from chromites. As may be seen from Tables 1 and 2 the process is able to achieve complete extraction of all PGM from the feed. PGM are leached from the residue and gas phase streams, losses of PGM to the condensate stream appear to be negligible.

EXAMPLE 3

[0092] This example shows that the PGM chlorides salts formed during the carbochlorination may be leached by water and by slightly acidified HCl solution from the residue and gas phase streams. The corrosive action of water and diluted HCl solutions is weak when compare to more concentrate HCl solutions. Therefore, the leached solutions are less charged in chemical species, other than PGM salts, which can possibly interfere in the subsequent metallurgical steps.

[0093] A ten-gram sample of the chromite CR-1 was contacted with a solution of NaCl. After drying the salt content of CR-1 was 5 % by weight. This material was loaded in the reactor and the temperature was raised to 660 °C in the presence of N₂. Once the reaction temperature was reached, 20 ml/min of Cl₂, 20 ml/min of CO and 100 ml/min of N₂ were flow through the

reactor. The mixture of gas was maintained in contact with the solid for 2 hours. Contrary to example 1, only the formation of a very small quantity of FeCl_3 was noted during the length of the experiment. The gas phase escaping the condenser area was quenched in water no precipitate was noted in the quenching vessel, although a red-yellow coloration appeared in the solution. This quench solution was used as a trap for the PGM transported in the gas phase.

[0094] After the two hours run, the reactor was cooled down to room temperature. Nitrogen was flushed in to the reactor during the cooling period. The solid left in the reactor, the residue, was transferred in a glass beaker placed on a hot plate. One hundred ml of water was added to the residue. The mixture was agitated for 15 minutes at 70 °C. After the agitation period, the mixture was filtered and the resulting clear solution was analysed for PGM by ICP-MS. The solid condensate (mostly FeCl_3) was recovered from the condenser area by washing with water. The condensate was digested using exactly the same digesting procedure as the one used for the residue. The water used as a trap for the PGM contained in the gas phase was analysed directly for the PGM.

[0095] Analysis of the condensate fraction by ICP-MS for the PGM did not lead to consistent results, most of the concentrations of PGM being below or close to detection limits. The poor detection limits was related to a matrix effect created by the high concentration of FeCl_3 in the analysed solution and to the small mass of FeCl_3 recovered from the condenser. Therefore, the presence of PGM in this particular fraction was estimated from the mass balance of the total PGM.

[0096] The distribution of the PGM in the residue and the gas phases are presented in Table 1 for the sample noted PGM-3. As may be seen from table 1 the sums of the PGM for the residue and the gas phases gives for: Pd 652 ppb, Pt 153 ppb, Ir 25 ppb, Os 7.3 ppb, Rh 69 ppb and Ru 45 ppb. The PGM concentrations obtained from the nickel sulphide fire-

assay, reported at the table 1, can be used as the 100 % recovery mark. Hence, the sums of PGM values in the residue and the gas phases were recalculated as per cent recovery in Table 2. It is to note that the analytical error is in the order of ± 15 %.

[0097] The recoveries vary from a minimum of 41 % for Os to a maximum of 129 % for Ir. Although the complete recoveries of PGM in the residue was not optimized herein in regard of the HCl content of the leaching solution it is clear from the above that a combination for which the PGM recovery in diluted HCl solution are comparable to ones obtained with HCl 10 M may be found by a person of ordinary skill in the art without undue experimentation . Such a combination is therefore encompassed by the present invention.

[0098] Although the invention has been described above with respect to a few representative examples and drawings, it will be evident in the person skilled in the art that it may be modified and refined in various ways. It is therefore wished to have it understood that the present invention should not be limited in scope, except by the terms of the following claims:

WHAT IS CLAIMED IS:

1. A method for recovering platinum group metals (PGM) from a feed material selected from the group consisting of chromite ore, chromite ore concentrate and PGM concentrate comprising
 - 5 a) dry chlorinating the material, having a homogenous grain-size, in a reactor maintained at a temperature of between about 250°C and about 750°C in the presence of a NaCl-FeCl₃ system acting as a catalyst so as to produce a solid material, a gaseous phase containing FeCl₃, and PGM chlorine salts that are soluble in water and HCl, whereby a portion of the
 - 10 PGM chlorine salts are contained in said solid material, and another portion of the PGM chlorine salts are contained in said gaseous phase; and
 - b) recovering PGMs from the PGM-chlorine-salts-containing solid material.
2. A method as recited in claim 1, further comprising the step of
15 recovering PGMs from the PGM-chlorine-salts-and-FeCl₃-containing gaseous phase.
3. A method as recited in claim 2, wherein the steps of recovering PGMs from the PGM-chlorine-salts-containing solid material and of PGMs from the PGM-chlorine-salts-and-FeCl₃-containing gaseous
20 phase are performed sequentially.

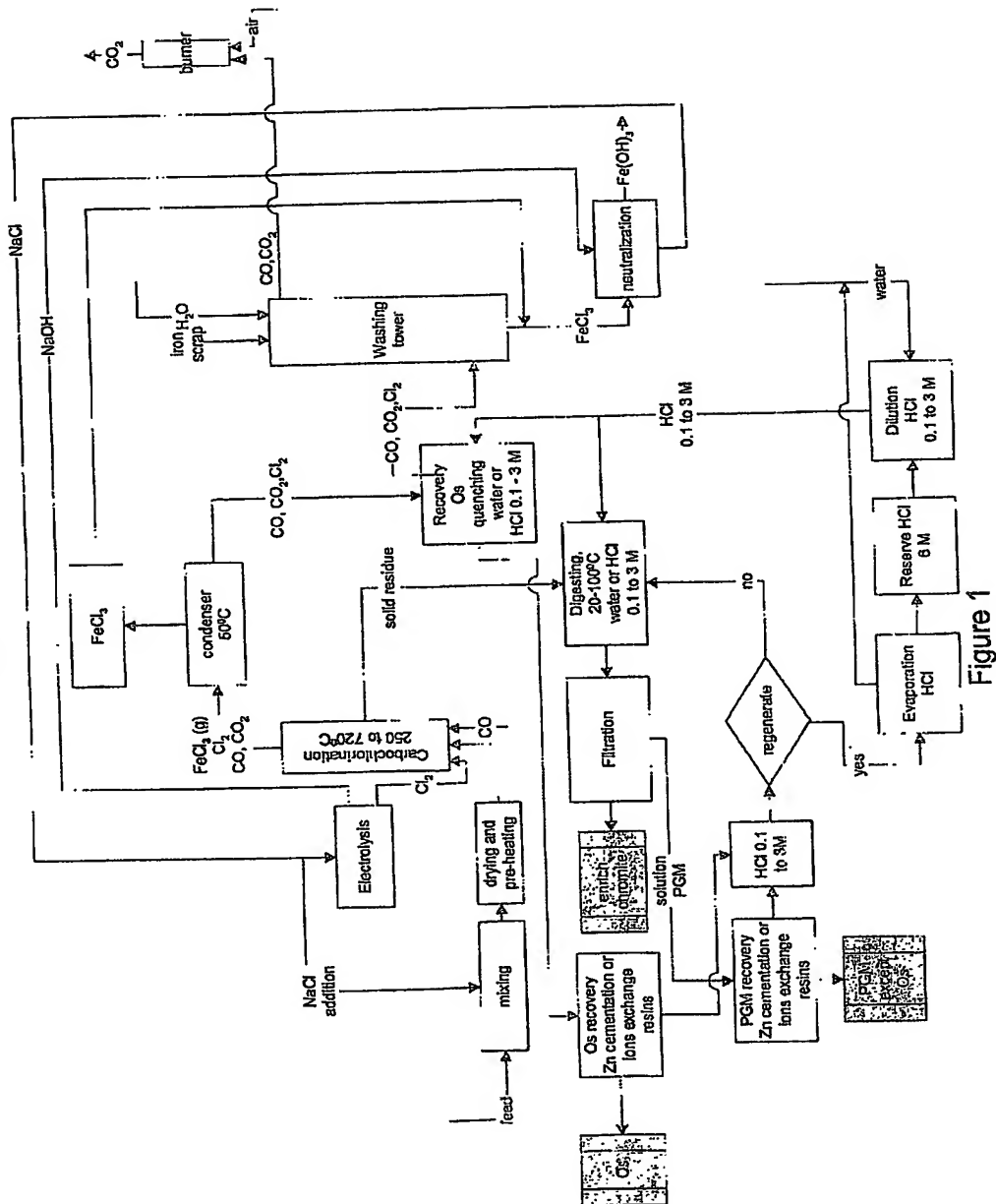


Figure 1

